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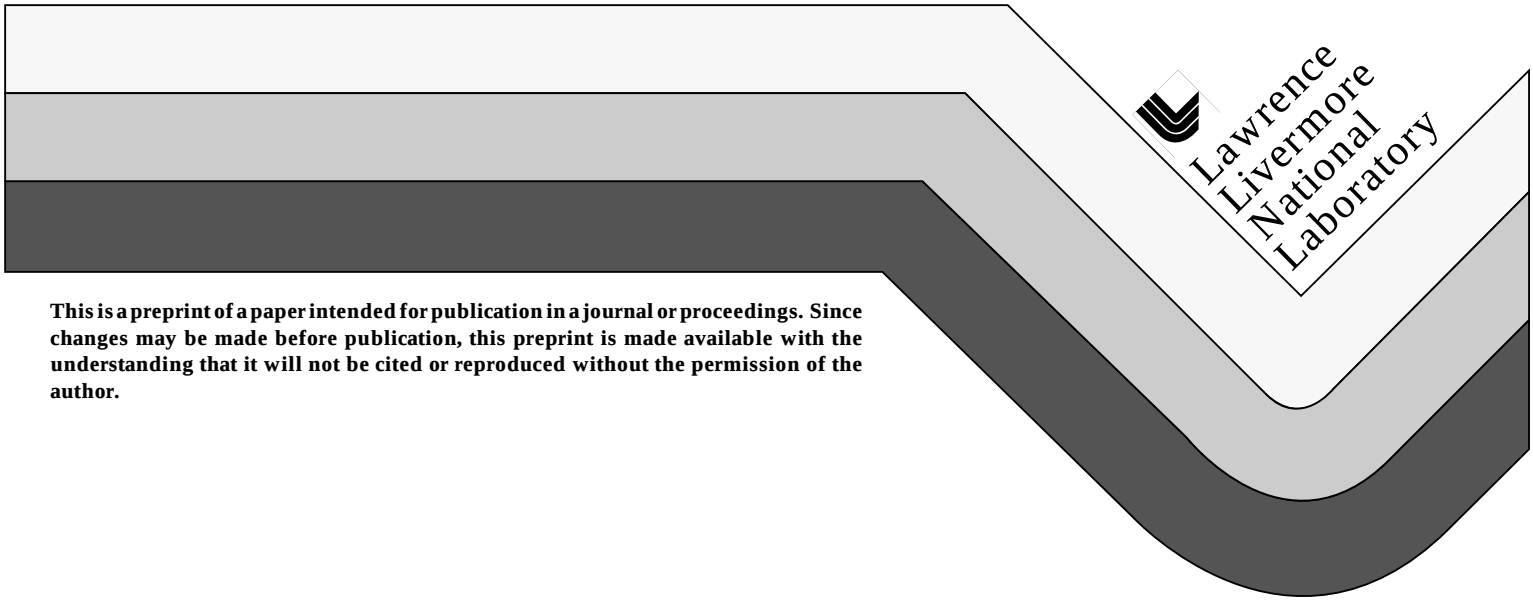

ELECTROCHEMICAL BEHAVIOR OF CARBON AEROGELS DERIVED FROM DIFFERENT PRECURSORS

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ABSTRACT

The ability to tailor the structure and properties of porous carbons has led to their increased use as electrodes in energy storage devices. Our research focuses on the synthesis and characterization of carbon aerogels for use in electrochemical double layer capacitors. Carbon aerogels are formed from the sol-gel polymerization of (1) resorcinol-formaldehyde or (2) phenolic-furfural, followed by supercritical drying from carbon dioxide, and subsequent pyrolysis in an inert atmosphere. These materials can be produced as monoliths, composites, thin films, powders, or microspheres. In all cases, the areogels have an open-cell structure with an ultrafine pore size (<100 nm), high surface area (400-1100 m^2/g), and a solid matrix composed of interconnected particles, fibers, or platelets with characteristic dimensions of 10 nm. This paper examines the effects of the carbon precursor and processing conditions on electrochemical performance in aqueous and organic electrolytes.

INTRODUCTION

The nanoengineering of materials is an area of intensive research because small clusters of atoms (1-100 nm) provide large interfacial areas and properties that range from the molecular to the bulk solid-state limits. Aerogels have a unique morphology in that *both* the covalently-bonded particles of the solid phase and the interconnected pores of the gas phase have nanometer-sized dimensions. This structure leads to extremely high surface areas (400-1100 m^2/g) with a large fraction of the atoms covering the surface of the interconnected particles. Sol-gel polymerization conditions can be used to engineer the particle size, particle interconnectivity, and pore size in these materials.

The polycondensation of (1) melamine with formaldehyde, (2) resorcinol with formaldehyde, and (3) phenolic with furfural are three proven synthetic routes for the formation of organic aerogels. The latter two materials can also be pyrolyzed in an inert atmosphere to give carbon aerogels [1-5]. Carbon aerogels are the first electrically conductive aerogels to be synthesized, and they are finding applications as electrodes in double layer capacitors used for energy storage or capacitive deionization [6-9]. In this paper, we discuss the chemistry-structure-property relationships of carbon aerogels derived from different polymeric precursors.

EXPERIMENTAL

The preparation of resorcinol-formaldehyde (RF) aerogels and their carbonized derivatives has been described elsewhere [4]. Briefly, resorcinol (1,3 dihydroxybenzene) and formaldehyde were mixed in a 1:2 molar ratio, respectively. Deionized/distilled water was added as the diluent and sodium carbonate as the base catalyst. After stirring to form a homogeneous solution, the mixture was poured into glass vials, sealed, and cured at elevated temperature (50-85 °C). Upon completion of the cure cycle, the crosslinked gels were exchanged with acetone and subsequently dried from supercritical carbon dioxide (T_c = 31°C; P_c = 7.4 MPa). This procedure resulted in the formation of monolithic RF aerogels which were subsequently pyrolyzed (600-1100 °C) in flowing nitrogen to form carbon aerogels.

Phenolic-furfural (PF) gels were prepared from a commercially available polymer solution (FurCarb UP520; QO Chemicals, Inc., West Lafayette, IN) [5]. This solution was composed of approximately a 50:50 mixture of a phenolic novolak resin dissolved in furfural. The Furcarb UP520 was diluted with 1-propanol and 10 parts per hundred resin catalyst (a mixture of aromatic acid chlorides; Q2001; QO Chemicals, Inc., West Lafayette, IN) was added. Solutions prepared with different amounts of diluent were then poured into glass vials, sealed, and cured for 7 days at 85 °C. A small amount of syneresis was observed during the cure cycle, allowing the gels to be easily removed. PF gels were supercritcally dried and pyrolyzed in the same manner as RF gels.

A variety of characterization techniques were used to analyze the carbon aerogels. Particle size and surface area were evaluated with transmission electron microscopy and gas adsorption techniques. Raman spectroscopy measurements were obtained in a backscattering configuration

using a 488-nm excitation. Transverse magnetic susceptibility measurements were carried out in a Superconducting Quantum Interference Design (SQUID) magnetometer. Samples were mounted in drinking straws and scanned in a 1-T field in a temperature range of 4-300 K.

Electrochemical studies were performed using a 64-channel Maccor battery tester. Experiments were done using circular (4.5 cm-diameter) Teflon® cells. Two identical (1.5 cm diameter, 1 mm thick) carbon electrodes were used in the cell and separated by 2 pieces of Whatman fiberglass filter paper (934-AH). Nickel foils were used as current collectors in aqueous cells, while aluminum foils were used as current collectors in cells with organic electrolytes. The whole assembly was sandwiched between 2 Teflon® plates and held together by 0.6 cm-diameter Teflon® screws. The aqueous electrolyte was 5M KOH. The organic electrolyte was 0.5 M tetraethylammonium tetrafluoroborate (Et_4NBF_4, Aldrich) in propylene carbonate. The operating voltage for the aqueous cell was 1 V per cell and that for the organic electrolyte was 3 V. The testing of aqueous cells was carried out under ambient conditions. The experiments with organic electrolytes were performed in a dry argon-atmosphere glove box (< 6 ppm water) at 16 ± 2°C. The charge/discharge current was 14 mA/cm^2 (geometric).

RESULTS AND DISCUSSION

The chemistry of resorcinol-formaldehyde(RF) and phenolic-furfural (PF) aerogels has been discussed previously [4,5]. Both reactions result in highly crosslinked gels that have an aromatic backbone. The RF aerogels lose ~50% of their starting mass upon carbonization at 1050 °C whereas the PF aerogels lose ~45%. Volumetric shrinkage in both cases can range from 60-75%, depending upon the exact formulation. Both precursors are considered to be non-graphitizable.

The structure and properties of RF-derived carbon aerogels are largely controlled by the [Resorcinol]/[Catalyst] (R/C) ratio of the starting solution. At R/C=50, carbon aerogels have particle diameters on the order of 7-9 nm with specific surface areas of ~800 m^2/g. In this type of aerogel, the particles are well-interconnected with the neck size approaching the particle diameter. In contrast, carbon aerogels synthesized at R/C=200, have lower surface areas (~600 m^2/g) and smaller necks between spherical particles of ~12 nm diameter. These structures have been explained in terms of the initial sol-gel chemistry and solution thermodynamics [10,11]. Interestingly, the specific surface area of these carbon aerogels is practically independent of the bulk density for samples prepared *at the same R/C ratio*. Thus, RF-derived carbon aerogels with a higher bulk density simply have more interconnected particles per unit volume than their low density counterparts.

In the case of the PF-derived carbon aerogels, transmission electron microscopy revealed interconnected platelets of irregular shape with characteristic sizes of 10-15 nm. The specific surface area of this material was also found to be largely independent of density at a given catalyst level. Figure 1 shows the specific surface area of RF aerogels, PF aerogels, and their carbonized derivatives as a function of density.

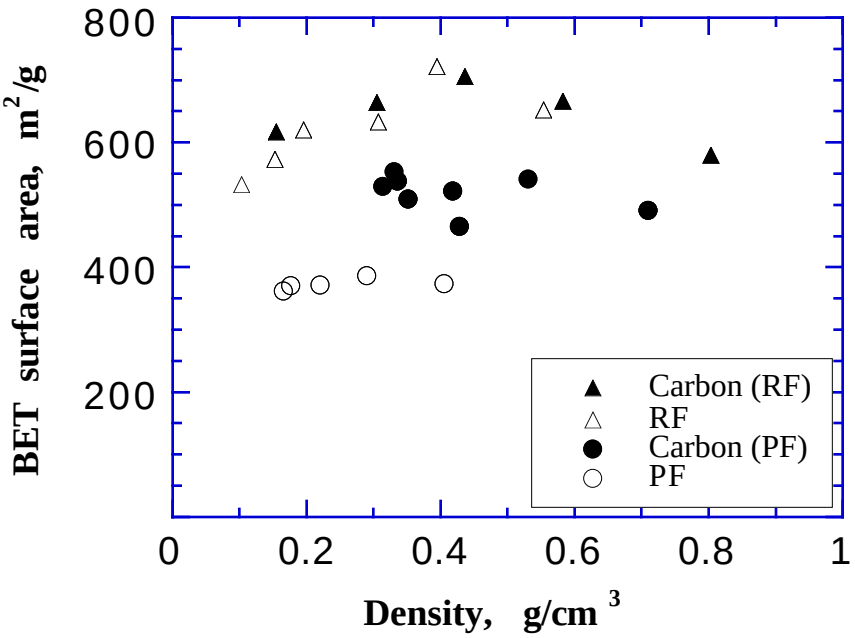

Figure 1. A comparison of the specific surface area of resorcinol-formaldehyde (RF) aerogels, phenolic-furfural (PF) aerogels, and their carbonized derivatives.

Raman spectroscopy was performed on carbon aerogels to probe the internal structure of the interconnected particles or platelets [12,13]. In both cases, a Raman-allowed E_{2g2} peak was observed near 1580 cm^{-1} (designated as the *G* band) while a Raman line attributable to in-plane disorder was observed near 1360 cm^{-1} (the *D* band). The in-plane microcrystallite size L_a was estimated from Knight's empirical formula, $L_a = 44 (I_G/I_D)$. For RF-based carbon aerogels pyrolyzed at 1050 °C, L_a is approximately 25 Å, independent of the bulk density or R/C ratio. For PF-based carbon aerogels pyrolyzed under the same conditions, L_a ranges from 25-35 Å with a slight density dependence. In both cases, the Raman data reveal that 25-35 Å wide graphene sheets are the underlying units in the carbon aerogel structure. The convoluted connection of the graphene sheet segments and the presence of defect sites are responsible for the micropores (< 2 nm) within the individual particles or platelets.

Magnetic susceptibility measurements were performed on carbon aerogels from 4-300 K as a function of bulk density and polymerization conditions [12,13]. In the low temperature regime, Curie-like behavior was observed and the number of spins per gram was determined for each specimen. Generally, carbon aerogels synthesized at R/C=50 exhibited a stronger temperature dependence at low temperature, and hence a larger number of unpaired spins per gram than their R/C=200 and R/C=300 counterparts at the same sample density. These data corroborate the BET surface area measurements and suggest that the R/C=50 samples are more highly disordered. Preliminary data on PF-based carbon aerogels show 2-3 times more spins per gram than RF-

based carbon aerogels (R/C=200) even though the BET surface areas exhibit the opposite trend. This discrepancy is under further investigation.

Because RF-derived and PF-derived carbon aerogels have high specific surface areas, they are potentially attractive as electrodes in double layer capacitors. Figure 2(a) shows the specific capacitance of the carbon aerogels in 5M KOH. The RF-derived carbon aerogels exhibit larger capacitance values than the PF-derived carbon aerogels at all densities. As expected, the specific capacitance of the RF-derived carbon aerogels depends upon the R/C ratio. At a fixed density, the following trend is observed for the specific capacitance: R/C=50 > R/C=200 > R/C=300.

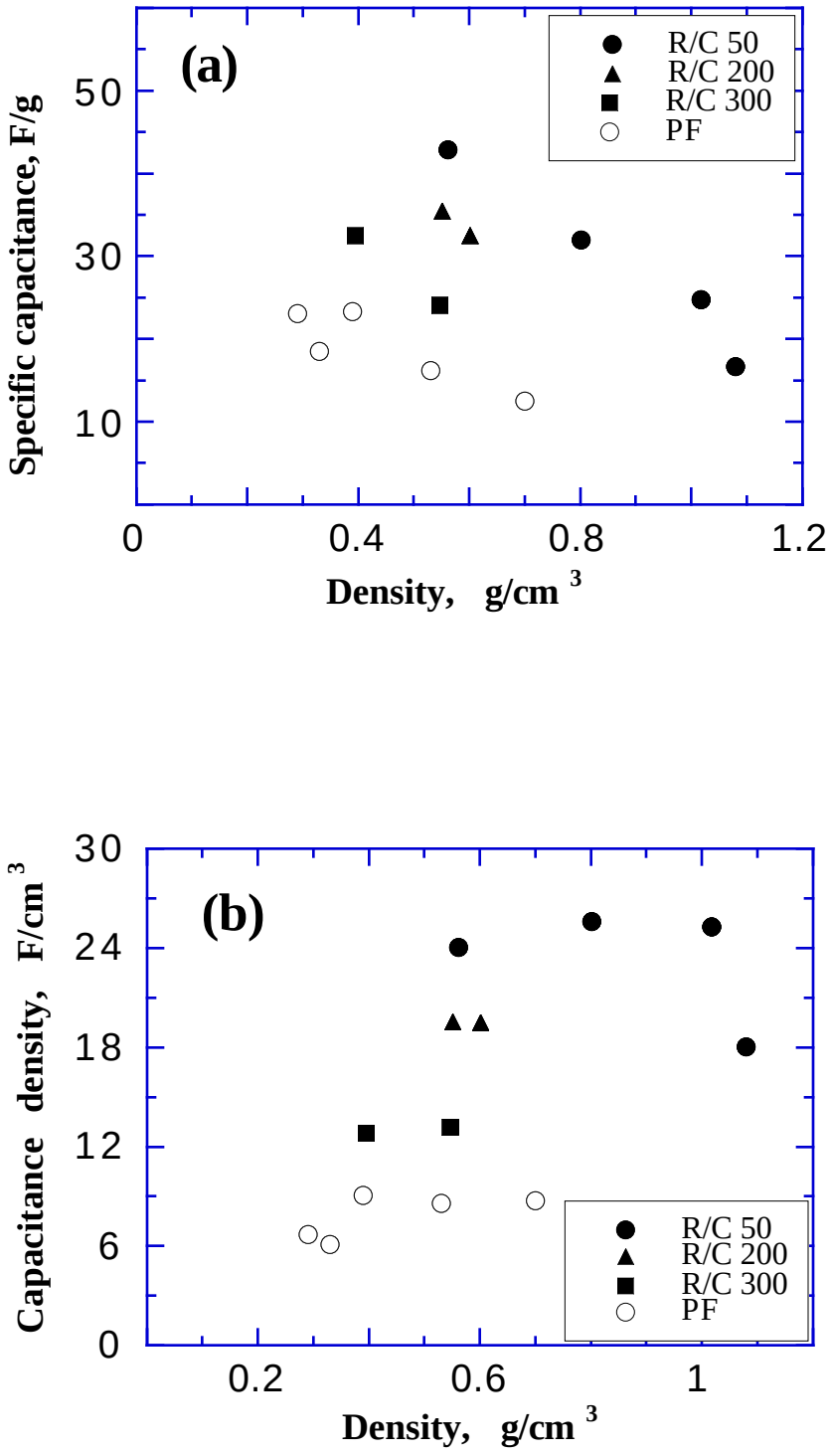

Figure 2. A plot of (a) specific capacitance vs. bulk density and (b) capacitance density vs. bulk density for carbon aerogels tested in 5M KOH.

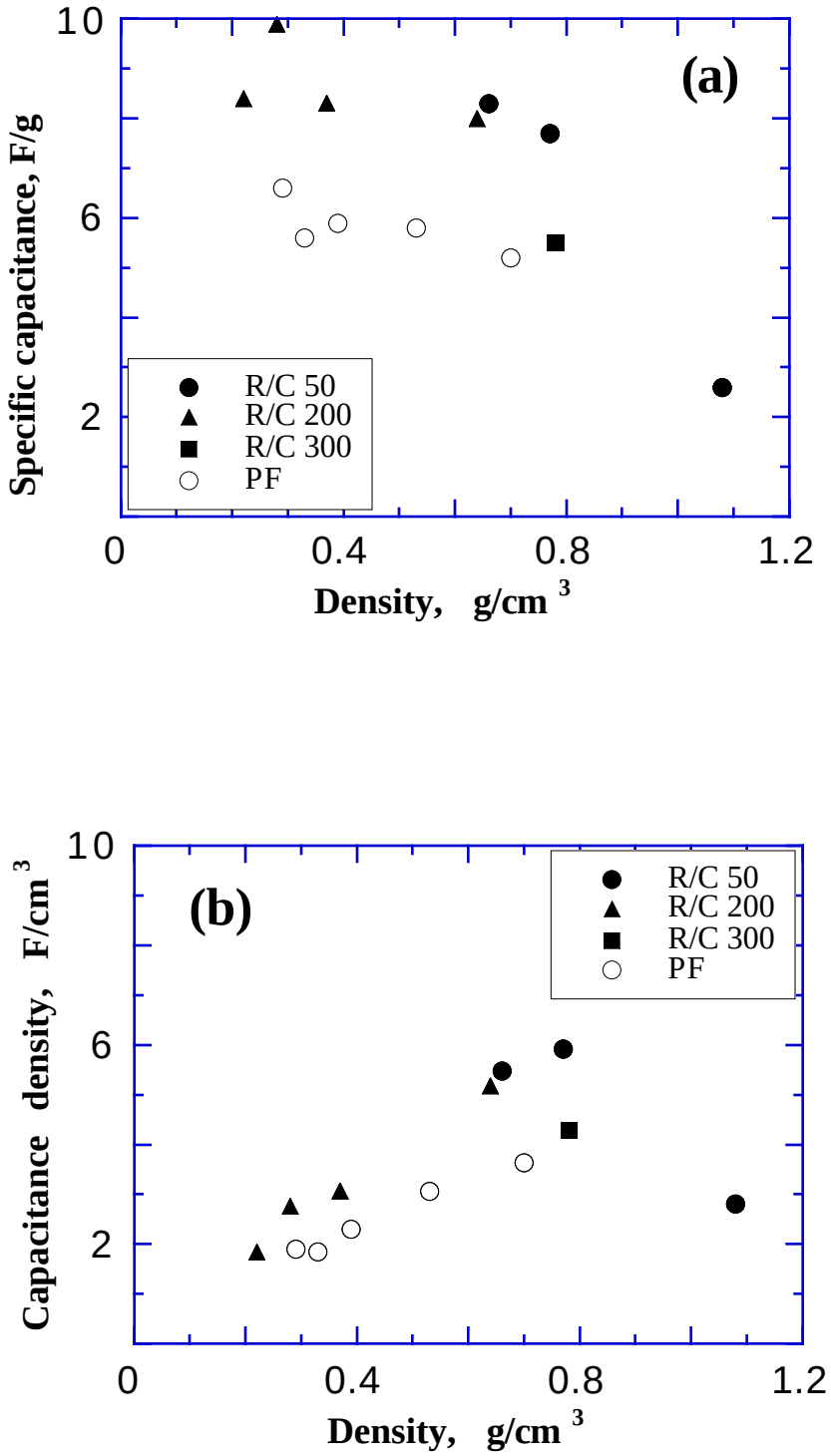

Figure 3. A plot of (a) specific capacitance vs. bulk density and (b) capacitance density vs. bulk density for carbon aerogels tested in 0.5M Et_4NBF_4/propylene carbonate.

The above data are in accord with the BET surface area measurements. In all cases, the specific capacitance decreases with increasing density of carbon aerogels. This effect can be explained in terms of the increased interconnectivity (particle coordination number) of the high density samples. The increased contacts lead to less accessible surface area per interconnected particle or per gram of carbon.

Figure 2(b) shows the capacitance density (F/cm^3) as a function of bulk density for the carbon aerogels derived from different precursors. There is a linear increase in capacitance density from 0-0.5 g/cm^3, followed by a plateau region in which maximum capacitance values of ~27 F/cm^3 and ~9 F/cm^3 are observed for the RF- and PF-derived carbon aerogels, respectively. Our data also show that the capacitance decreases at very high densities, suggesting that the average pore size is becoming too small for double layer formation. Based upon permeability data, the RF-derived carbon aerogels have an average mesopore size of ~3.5 nm at 1.1 g/cm^3.

Figures 3(a) and 3(b) show the specific capacitance and capacitance density of carbon aerogels in the organic electrolyte. The trends are similar to the aqueous case, although the magnititude of the capacitance is 3-4 times lower. A sharp decrease in capacitance density is also observed for the highest density specimen, suggesting that the pore size is becoming too small to accomodate the double layer. The energy density E of an individual cell can be calculated as follows

$$E = 0.5\ CV^2 \qquad [1]$$

where C equals capacitance and V equals operational voltage. In the case of the organic electrolyte, a nine-fold increase in energy density might be expected because of the higher cell voltage in comparison to the aqueous case (3V vs. 1V). The increased energy density, however, is only 2-3 times the aqueous case because of the decreased capacitance associated with the larger ionic species and the lower dielectric constant of the organic electrolyte.

SUMMARY

Carbon aerogels can be synthesized from different polymeric precursors to give porous electrodes with low electrical resistivity, controllable pore size, and high surface area. RF-derived carbon aerogels provide higher capacitance than PF-derived carbon aerogels in both aqueous and organic electrolytes. Maximum values of ~27 F/cm^3 and ~6 F/cm^3 were achieved in these respective electrolytes.

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